Photocatalytic hydrogen evolution over the isostructural titanates: \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) modified with metal oxide nanoparticles

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**Abstract**

Isostructural titanates exhibiting rectangular tunnel structure with the general formula \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) and \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) were synthesized by solid state and sol-gel methods. The structural, morphological, optical, textural and electrical properties of the materials were characterized by XRD, SEM, UV-vis, BET and EIS. The photocatalytic activity for hydrogen evolution of the materials was evaluated under UV light. \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) exhibited higher activity (120 \( \mu \text{mol/g.h} \)) than \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) (30 \( \mu \text{mol/g.h} \)), and it was attributed to the distortion of the octahedrons in \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \), which increases the recombination of charges in the material. Additionally, the 1D dimension obtained in \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) promotes a better charge separation, transport and utilization in this phase. The activity of the materials was enhanced with the incorporation of metal oxide nanoparticles \( \text{MO} (\text{M} = \text{Cu}, \text{Ni}) \) as cocatalysts. The activity of \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) increased 10 times with the addition of \( \text{CuO} (240 \mu\text{mol/g.h}) \), while the activity of \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) increased 3.5 times (416 \( \mu\text{mol/g.h}) \). This improvement in the photocatalytic activity of the isostructural titanates was attributed to the formation of a p-n heterostructure between n-type titanates and p-type CuO, which promoted an enhanced charge separation, transference and utilization.

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**Introduction**

Since the Fujishima and Honda study in 1972 \([1,2]\), heterogeneous photocatalysis has attracted attention for different novel applications. One of these includes its use for hydrogen generation from water splitting. This process involves an endothermic reaction where 2 electrons are transferred, requiring 1.23 eV for every electron. The energy required for this process can be achieved through heterogeneous photocatalysis \([3]\). For this reason, traditional and novel photocatalysts based on semiconductor materials have been developed. Simple metal oxides, such as \( \text{TiO}_2 \) \([4–7]\), \( \text{ZnO} \) \([8–10]\), \( \text{ZrO}_2 \) \([11,12]\), \( \text{WO}_4 \) \([13,14]\), and other oxides belonging to the families of perovskites \([15–17]\), pyrochlores \([18–20]\),

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ilmenites [21–23], tunnel structured materials [24–26], among others, have exhibited suitable properties for the hydrogen evolution process. The recombination of the photogenerated charges in the bulk and the surface of the materials represent a problem that reduces significantly the photocatalytic activity.

In order to reduce the recombination of charges, several strategies have been employed. This includes the development of novel morphologies [2,24], the increase in the surface area and the number of active sites for the catalytic reactions, and the control of the conditions of synthesis for obtaining suitable optical and electronic properties to perform the reduction of water. Other strategy consist in the use of metal oxides as cocatalysts (such as CuO, FeO, NiO, RuO2) [27–29], to promote the efficient charge separation, transport and utilization. Cocatalysts increase the lifetime of the photogenerated charges and enhance the overall yield of the photocatalytic reaction. Tunnel structured titanates have attracted the interest of researchers in the photocatalytic field due to their suitability to obtain 1D morphologies that promotes a more efficient separation of the photogenerated charges [30,31]. In the tunnel structured materials, the heavily distorted TiO6 octahedrons allows a higher efficiency of the photoexcited charge separation process [32–34]. For this reason, considerable number of research works about these materials have been reported recently for photocatalytic applications [35–37].

Na2Ti6O13 is a material with tunnel structure that has been synthesized for different methods and applied for photocatalytic hydrogen production and degradation of organic compounds [38–40]. In recent reports, the activity of this material has been improved with the addition of CuO [40] and RuO2 [41] as cocatalysts. Another group of tunnel structured titanates is the solid solution with general formula Ba3xLi2x/3Ti6(3–x/4)yO13, with 0.32 ≤ x ≤ 0.42 and 0 ≤ y ≤ 0.2, present in the system BaO-Li2O-TiO2. The isothermal phase diagram of this system was studied by Suckut et al. [42], reporting the crystalline structure of the composition Ba3Li2x/3Ti16/3O13. This phase has been applied for catalytic combustion of methane [43] and photocatalytic degradation of 2, 4-dinitroaniline [44]. Ba3Li2x/3Ti16/3O12 is an isostructural material to Na2Ti6O13, and its conduction band is suitable to perform the reduction of water. To this date, there are no reports of the photocatalytic activity for hydrogen evolution using this phase. For this reason, in this work we prepared this material by two different methods and evaluated the activity for photocatalytic hydrogen generation. Also, we present a comparative and integral study of the structural, optical, textural and photocatalytic activity of Ba3Li2Ti6O20 and the isostructural phase Na3Ti6O13, and the improvement in their photocatalytic activity with the addition of copper and nickel oxides as co-catalysts.

**Experimental**

**Synthesis of Na2Ti6O13 and Ba3Li2Ti6O20 by solid state reaction and sol-gel method**

For the solid state synthesis of Na2Ti6O13, Na2CO3 anhydrous (99.9% DEQ) and TiO2 (Degussa P25) were mixed in equimolar proportions according to the phase diagram [42] in an agate mortar using acetone as dispersant. The same methodology was used for the preparation of Ba3Li2Ti6O20, where BaCO3 (>99% Sigma Aldrich), Li2CO3 (99.9% Fermont) and TiO2 (Degussa P25), where mixed in a relation 32-16-78 mol% respectively, to obtain the previously reported composition [44]. In order to reduce lithium loss by volatilization, tablets were fabricated in a Carver hydraulic press at 6 metric tons. The materials were transferred into a platinum crucible and thermally treated in air at 1100 °C for 12 h for the Ba3Li2Ti6O20 and 800 °C for the Na2Ti6O13, using a heating rate of 3 °C min⁻¹.

Sol-gel synthesis of Na2Ti6O13 was performed following the methodology reported previously [35]. A stoichiometric amount of titanium butoxide (97% Sigma Aldrich) was dissolved in ethanol anhydrous. Separately, sodium acetate anhydrous (99.9% Fermont) was dissolved in water and ethanol and added drop by drop into the flask containing titanium butoxide. Similarly, Ba3Li2Ti6O20 was prepared using the methodology reported by Hernandez et al. in 2002 [44], where barium acetate (99.8% Fermont) and titanium butoxide were dissolved in ethanol and glacial acetic acid (Fermont). In other vessel, lithium acetate (99.9 Sigma Aldrich) were dissolved in water and then added drop to drop to the first solution.

Both flasks were refluxed at 70 °C during 72 h under constant stirring and the resulting gel was dried until complete evaporation of solvents. Finally, the obtained gels were thermally treated at 900 °C to ensure the complete crystallization.

**Deposit of MO (M = Cu, Ni) as co-catalysts by wet impregnation method**

Metal oxide particles were deposited on Ba3Li2Ti6O20 and Na2Ti6O13 by the method of wet impregnation [40]. Metallic acetates (cupric acetate, Fermont, and nickel acetate, DEQ) in different amounts (0.5–5% in weight) were dissolved in ethanol. The respective mass fraction of the photocatalyst was added and the suspension was kept under continuous stirring for 1 h. After this time, the temperature was kept at 80 °C until complete evaporation. Finally, the samples were thermally treated at 400 °C for 2 h to obtain the metal oxides.

**Characterization**

Phase formation of the materials was studied by X-ray diffraction using a Bruker D8 Advance diffractometer with a wavelength of λ = 1.5406 Å of Cu-Kα radiation. Oxidation state of MO particles impregnated was analyzed in a Perkin Elmer Phi 560 XPS/Auger System doing the data treatment with the AA analyzer software. The morphological and elemental analysis of the samples was explored with a Scanning Electron Microscope JEOL 6490LV in the secondary electron mode under high vacuum at 20 kV coupled to an Energy Dispersive X-ray Spectroscopy analyzer.

Specific surface area was measured by N2 physisorption through the BET method using a Belsorp II mini (Bel Japan) equipment and the optical properties were analyzed in a range of 200–800 nm in a UV-vis NIR spectrophotometer Cary 5000 coupled to an integration sphere for diffuse reflectance.
Photoluminescence measurements were evaluated at room temperature in a fluorescence spectrophotometer Agilent Cary Eclipse, using a scan speed of 1000 nm/min and a wavelength of excitation of 380 nm for \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and 350 nm for \( \text{Na}_2\text{Ti}_6\text{O}_{13} \).

Additionally, the electrochemical characterization of the materials was performed in a potentiostat-galvanostat Metrohm Autolab with a three electrode quartz cell. Ag/AgCl was used as reference electrode, platinum as counter electrode, and the working electrode was prepared using a slurry of the sample of interest (0.2 g), terpineol (0.05 g) and ethanol (2 mL). The slurry was screen printed on an ITO substrate (1 cm\(^2\) of active working area); and then, dried and calcined at 400 °C for 30 min. The three electrodes were immersed in an electrolyte solution of 0.5 M \( \text{Na}_2\text{SO}_4 \) (pH 7) and bubbled with nitrogen for removing the oxygen. Mott-Schottky curves were performed under dark conditions through an impedance spectroscopy study at 1000 Hz.

**Photocatalytic hydrogen evolution**

Hydrogen evolution was tested using a 250 mL slurry Pyrex reactor containing 200 mL of deionized water and 0.1 g of catalyst. An UV pen-lamp (\( \lambda_{\text{max}} = 254 \text{ nm}, \chi_{\text{max}} = 2.2 \text{ mW/cm}^2 \)) was immersed in the suspension into a quartz tube.

Hydrogen production was measured in-situ taking samples every 30 min in a Trace GC Ultra Thermo Scientific gas chromatograph equipped with a Thermal Conductivity Detector (TCD), a fused silica capillary column (30 m × 0.53 mm) and nitrogen (ultra high purity, Infra) as carrier gas.

**Results and discussion**

In this section, we present the results of the characterization of the titania phases synthesized by solid state and sol-gel method pure and modified with the optimal loading (2%) of CuO and NiO nanoparticles. For facility, in some of the Figures the identification of the phases \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) is presented as BLTO and NTO, respectively, and the solid state and sol-gel methods as SS and SG.

**X-ray diffraction**

Fig. 1 (a) and (b) shows the XRD patterns of \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) synthesized by solid state reaction and sol-gel method. The materials exhibited crystalline patterns, with well-defined peaks. Both materials crystallized in a monoclinic structure with space group C2/m, according to the JPDF cards 049-0189 and 01-073-1398, respectively.

The crystal structure of \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) is isostructural to \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) [Fig. 2]. In this structure, three \( \text{TiO}_6 \) octahedral form edge-sharing trimers, which share corners with other trimers to form infinite ribbons in a zig-zag arrangement. The Ba and Na atoms are located inside the tunnels. Lithium partially substitutes titanium in one of the three octahedral sites in the structure [45,46]. The catalytic activity is promoted by this tunnel structure, due to the octahedral distortion, which produces dipole moments directed to the center of the tunnel, enhancing the separation of the photogenerated charges.

In the Rietveld refinement of these materials previously reported by Torres-Martinez et al. [35,46] the atomic fractional coordinates and the sites for Na, Ti, O, Ba and Li are discussed.

In \( \text{Na}_2\text{Ti}_6\text{O}_{13} \), one of the oxygen atoms is refined in the site 2a, while in \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \), in the site 2b.

Additionally, differences in the cations nature and size cause small variations in the bond lengths, the lattice parameters and the reflections observed in the patterns presented in Fig. 1 (a) and (b).

In Fig. 1 (a), it is observed that the patterns of the powders of \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) prepared by solid state and sol-gel are identical and exhibit a strongest peak at 31.6 °, corresponding to the plane (112). The crystallite size of \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) samples was calculated through the Scherrer equation. The values calculated were 39.6 and 38.7 nm for the materials obtained by solid state and sol-gel. In both synthesis, the materials were obtained at 1100 °C, promoting similar crystallite size.

The XRD patterns of \( \text{Na}_2\text{Ti}_6\text{O}_{13} \), presented in Fig. 1 (b), are also similar, and the strongest peak is located at 11.8 °, which corresponds to the plane (200). The crystallite sizes calculated for \( \text{Na}_2\text{Ti}_6\text{O}_{13} \), obtained by solid state and sol-gel were 132 and 137 nm. The temperature used for the obtention of the pure phase by the two methods was 800 °C. The differences in the crystallite size calculated in the phases obtained by different methods was no significant.

In Fig. 1 (a) and (b) it is also included the XRD patterns of titania phases modified with 2% of metal oxide nanoparticles (MO = Ni, Cu). Due to the low concentration of the metal oxides, no additional peaks corresponding to copper or nickel oxide were observed in the XRD patterns of \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) and \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \). Further surface analysis of the phases by SEM, EDS and XPS were performed in order to corroborate the presence of the metal oxide nanoparticles in the surface of the titania photocatalysts.

**Scanning electron microscopy**

Fig. 3 shows the SEM images of pure and modified \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) samples. \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) exhibited grains of irregular shape with particle size smaller than 1 μm, while \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) showed the formation of well-defined nanobelts with a regular size of around 1 μm. This is a common feature of \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) powders and a variety of 1D structures have been prepared from this material [32]. In both methods of synthesis, the phases \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) exhibited similar morphologies, due to the temperature needed for the phase formation by the two methods was equal (\( T_{\text{formation}} \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} = 1100 °\text{C} \), and \( T_{\text{formation}} \text{Na}_2\text{Ti}_6\text{O}_{13} = 800 °\text{C} \)).

Fig. 3 also presents the morphology of the phases modified with 2% of NiO and CuO. From these images, we assume the NiO and CuO particles deposited on the surface of the isostructural titanates by the impregnation method are in the nanometric scale. In some of the images, NiO and CuO nanoparticles can be appreciated deposited on the surface of the isostructural titanates.

In order to corroborate the presence of MO (M = Cu and Ni) particles on the surface of the photocatalysts, an elemental analysis by EDS was carried out. Fig. 4 presents the distribution of copper and nickel on \( \text{Ba}_3\text{Li}_2\text{Ti}_8\text{O}_{20} \) and \( \text{Na}_2\text{Ti}_6\text{O}_{13} \) modified with 2% of NiO and CuO. As can be seen in this
Figure, the dispersion of NiO and CuO particles on the surfaces of the tunnel structured titanates is homogeneous. A quantitative analysis of the content of the metal oxides deposited is presented in Table 1. In this table, the weight percent of MO deposited theoretically is also included. The obtained values of metal oxides in the samples is slightly smaller to the theoretical amount, due to weight losses during the impregnation process.

(a) Ba$_3$Li$_2$Ti$_8$O$_{20}$  
(b) Na$_2$Ti$_6$O$_{13}$

Fig. 1 – XRD patterns of the tunnel structured titanates: (a) Ba$_3$Li$_2$Ti$_8$O$_{20}$ and (b) Na$_2$Ti$_6$O$_{13}$, and their modification with 2% of metal oxide nanoparticles (MO = Ni, Cu).

Fig. 2 – Crystalline structure of (a) Ba$_3$Li$_2$Ti$_8$O$_{20}$ and (b) Na$_2$Ti$_6$O$_{13}$. 
X-ray photoelectron spectroscopy

XPS analysis were carried out in order to obtain information of the chemical species present on the surface of the samples and to corroborate the deposition of the metal oxide nanoparticles over the tunnel structured titanates. Two representative samples were analyzed: Ba$_3$Li$_2$Ti$_8$O$_{20}$ SS 2% CuO and Na$_2$Ti$_6$O$_{13}$ SG 2% NiO.

Fig. 5 (a) and (c) shows the XPS survey of the samples, where is confirmed the presence of Ba, Li, Ti, O and Cu in the first sample, and Na, Ti, O and Ni in the second.

In Fig. 5 (b) is presented the Cu 2p spectra of the first sample, where it was possible to identify two signals at 933 and 953 eV, corresponding to Cu 2p 3/2 and Cu 2p 1/2, respectively. Two strong satellite peaks were observed at 943 and 963 eV. These signals are characteristic of Cu$^{2+}$ and confirmed the presence of CuO in the sample [47,48].

Fig. 5 (d) shows the Ni 2p spectrum of the second sample with two main peaks at 855 eV and 856 eV. Also, a satellite peak is observed at 862 eV. The signals were assigned to nickel oxidized species (NiO) in the sample [49,50].

UV-vis diffuse reflectance

The diffuse reflectance spectra of Ba$_3$Li$_2$Ti$_8$O$_{20}$ and Na$_2$Ti$_6$O$_{13}$ modified with NiO and CuO nanoparticles are presented in Fig. 6. In these figures, the absorption range of the materials is observed, and it begins at wavelengths below 350 nm. This
corresponds to an UV absorption, characteristic of the studied isostructural titanates [40].

The deposition of the metal oxide nanoparticles on the surface of titanates modified the absorption properties of the materials. Transition metal oxides promoted an absorption in the visible range due to the nature of their electronic structure and their characteristic d–d transitions. Due to this, the modified titanates exhibited an increased absorption, reflected in smaller band gaps.

Table 2 summarizes the calculated band gaps. Band gap of the materials were found in the range of 3.0–3.5 eV.

### Photoluminescence spectroscopy

Photoluminescence analysis were carried out in order to study the efficiency of separation and transference of the photogenerated charges, and to understand the effect of the metal oxide nanoparticles deposited on the surface of the photocatalysts, associating the emission with the recombination of electrons and holes. Fig. 7 shows the photoluminescence spectra of pure and modified (a) Ba₃Li₂Ti₈O₂₀ and (b) Na₂Ti₆O₁₃. In the emission spectra of the structured titanate materials, Ba₃Li₂Ti₈O₂₀ synthesized by sol gel exhibited higher emission intensity compared to the material obtained by solid state, while in Na₂Ti₆O₁₃, the opposite behavior was observed. The highest photoluminescence emission was associated with a highest recombination rate in the samples. In both titanates, the photoluminescence emission was reduced with the incorporation of metal oxide particles as cocatalysts. This implies that the CuO and NiO nanoparticles are promoting a better charge separation and transport in the interface of titanates with metal oxides. The lowest photoluminescence emissions were observed in the samples modified with CuO, due to the band alignment and p-type nature of this oxide, which allows a suitable coupling, charge separation and transference in the interface of the heterostructure with n-type barium and sodium titanates. The formed n-p heterostructure improves the kinetic of the photogenerated charges.
and reduce the recombination process, enhancing the efficiency in the use of the electrons and holes in the photocatalytic reactions.

**Electrochemical characterization**

As it is well known, the flat band potential influences the photoresponse of a semiconductor. A more negative character of this parameter promotes a better charge separation in the material. For this reason, in this work an electrochemical impedance spectroscopy study of representative samples (Ba$_3$Li$_2$Ti$_8$O$_{20}$ SS and Na$_2$Ti$_6$O$_{13}$ SG pure and with 2% CuO) was performed. These samples correspond to the materials that exhibited the lowest photoluminescence emission in the previous study. **Fig. 8** shows the Mott–Schottky plots of these bare and modified titanates. The flat band potential ($E_{FB}$) was calculated from these plots. The intercept at X of the plot of $C/C_0^2$ versus $E$ is the value of the flat band potential. Both titanates exhibited positive slopes, characteristic of n-type semiconductors. As it is shown in this Figure, the conduction band of the titanates become more negative with the addition of metal oxides. A more negative conduction band in a

**Fig. 5** – XPS spectra of (a, b) Ba$_3$Li$_2$Ti$_8$O$_{20}$ SS 2% CuO and (c, d) Na$_2$Ti$_6$O$_{13}$ SG 2% NiO.

**Fig. 6** – UV-vis diffuse reflectance spectra of (a) Ba$_3$Li$_2$Ti$_8$O$_{20}$ and (b) Na$_2$Ti$_6$O$_{13}$ modified with NiO and CuO nanoparticles.
material is more favorable for the hydrogen evolution. Additionally, the slope in the samples modified with metal oxides increased, which implies that the charge carrier density is higher in the modified samples compared to the bare titanates.

The flat band potential calculated for Ba$_3$Li$_2$Ti$_8$O$_{20}$ SS 2% CuO was $-0.5$ V, while for Na$_2$Ti$_6$O$_{13}$ SG 2% CuO, $-0.6$ V. These results imply that the sample Na$_2$Ti$_6$O$_{13}$ SG 2% CuO exhibits a higher photoresponse and that the processes of charge separation and transport in this sample are improved, which is beneficial for its photocatalytic performance.

**Photocatalytic activity for hydrogen evolution**

The evaluation of the photocatalytic activity for hydrogen evolution of pure and modified Ba$_3$Li$_2$Ti$_8$O$_{20}$ and Na$_2$Ti$_6$O$_{13}$ under UV light is discussed in this section. Fig. 9 shows the hydrogen production exhibited by the samples during 3 h. As it is shown in these figures, all samples exhibited stable activity under UV light. From these curves, the average hydrogen production rate of the samples was calculated and summarized in Table 2.

<table>
<thead>
<tr>
<th>Tunnel structured material</th>
<th>Metal oxide</th>
<th>Surface area (m$^2$/g)</th>
<th>Band gap (eV)</th>
<th>H$_2$ evolution ($\mu$mol/gh)</th>
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<tr>
<td>Ba$_3$Li$_2$Ti$<em>8$O$</em>{20}$ SS</td>
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<td></td>
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<tr>
<td></td>
<td>2% NiO</td>
<td></td>
<td>3.0</td>
<td>196</td>
</tr>
<tr>
<td>Ba$_3$Li$_2$Ti$<em>8$O$</em>{20}$ SG</td>
<td>Bare</td>
<td></td>
<td>3.0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>2% CuO</td>
<td></td>
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<td>41</td>
</tr>
<tr>
<td></td>
<td>2% NiO</td>
<td></td>
<td>3.0</td>
<td>54</td>
</tr>
<tr>
<td>Na$_2$Ti$<em>6$O$</em>{13}$ SS</td>
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<td></td>
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<td>90</td>
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<td>250</td>
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<tr>
<td>Na$_2$Ti$<em>6$O$</em>{13}$ SG</td>
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<tr>
<td></td>
<td>2% CuO</td>
<td></td>
<td>3.3</td>
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<tr>
<td></td>
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</table>

First, we evaluated the effect of the method of synthesis (solid state and sol-gel) on the photocatalytic activity of the tunnel structured titanates. In Ba$_3$Li$_2$Ti$_8$O$_{20}$, the samples prepared by solid state and sol-gel exhibited similar activity: 25 $\mu$mol/gh and 30 $\mu$mol/gh, respectively. In Na$_2$Ti$_6$O$_{13}$, the use of the sol-gel method allowed the obtention of a higher activity (120 $\mu$mol/gh) compared to the traditional solid state route (90 $\mu$mol/gh). This difference in the activity could be attributed to the soft conditions employed in the sol-gel synthesis, which allows a controlled nucleation and growth of the material. Due to this, the crystallite size of the sample obtained by sol-gel (137 nm) was slightly higher to the obtained by the sample prepared by solid state (132 nm). The higher crystallinity obtained in the sol-gel sample promoted a higher photocatalytic activity.

Ba$_3$Li$_2$Ti$_8$O$_{20}$ samples exhibited lower photocatalytic activity compared to Na$_2$Ti$_6$O$_{13}$. Though these materials are isostructural, the bond lengths in Ba$_3$Li$_2$Ti$_8$O$_{20}$ [36] are higher compared to the calculated in Na$_2$Ti$_6$O$_{13}$ [37]. This generates a higher distortion in Ba$_3$Li$_2$Ti$_8$O$_{20}$ octahedrons, promoting a higher recombination of charges in this material and a lower photocatalytic activity. Additionally, the powders obtained of the phase Na$_2$Ti$_6$O$_{13}$ exhibited a characteristic 1D morphology, in contrast to the grains observed in Ba$_3$Li$_2$Ti$_8$O$_{20}$. Materials with morphologies in 1D exhibit an improved charge separation, transport and utilization, leading to higher photocatalytic efficiencies.

The incorporation of metal oxide nanoparticles on the surface of the tunnel structured titanates improved the photocatalytic performance of the materials.

In both phases, the materials modified with CuO nanoparticles exhibited the highest activities. Ba$_3$Li$_2$Ti$_8$O$_{20}$ synthesized by solid state exhibited an activity of 30 $\mu$mol/gh and it increased 10 times with the addition of CuO (240 $\mu$mol/gh). In the case of the phase Na$_2$Ti$_6$O$_{13}$ prepared by sol-gel, the pure material showed an activity of 120 $\mu$mol/gh, and it increased 3.5 times with the incorporation of copper oxide (416 $\mu$mol/gh). This is the sample with the highest photocatalytic efficiency, and corresponds to the sample with the lower emission exhibited in the photoluminescence analysis.
The major photocatalytic activity of this sample is attributed to the formation of a n-p heterostructure between n-type Na$_2$Ti$_6$O$_{13}$ and p-type CuO, which allows an efficient separation and transference of the photogenerated charges in the interface of the semiconductors, promoting an improved photocatalytic activity. This mechanism is represented in Fig. 8 – Mott-Schottky plots of (a) Na$_2$Ti$_6$O$_{13}$ and (b) Ba$_3$Li$_2$Ti$_8$O$_{20}$.

Fig. 9 – Photocatalytic performance of the tunnel structured titanates synthesized by solid state and sol gel synthesis.
Based on this, the irradiation of the tunnel structured titanate with UV light, promotes the generation of electron and hole pairs. The holes in the valence band of the titanate are transferred to the valence band of CuO, where the water oxidation reaction is performed. Meanwhile, in the conduction band of titanate, the electrons reduce protons to complete the hydrogen evolution.

Representative samples were photocatalytically tested under simulated solar radiation (see Fig. S2). In all cases, the activity of the materials decreased at least in a 60%. This correspond to the expected, due to the low portion (4%) of UV light present in the simulated solar radiation, and considering that the titanate photocatalysts are active only under UV light.

For the best of our knowledge, the activities obtained by the photocatalysts developed in this work are competitive with similar materials reported in the literature.

Stability of the photocatalysts
To analyze the stability, tests of representative samples were performed (See Fig. S3). As shown in this figure, the activity of the materials remains stable after 3 cycles of reaction. This is indicative that there is an appropriate coupling between the titanate and the metal oxides, and that the materials are not being corroded, reduced or lost in the solution. To corroborate this, the as prepared and post-reaction samples were characterized by X-ray diffraction, SEM and XPS.

a) XPS

Fig. S4 (a) shows the XPS spectra of Na$_2$Ti$_6$O$_{13}$ SS modified with 2% of CuO. Two signals were identified at 933 eV and 953 eV, corresponding to Cu 2p 3/2 and Cu 2p 1/2 (Cu$^{2+}$) signals. In the Ba$_3$Li$_2$Ti$_8$O$_{20}$ 2% NiO sample, two peaks at 855 eV and 856 eV representative of Ni 2p 3/2 and Ni 2p 1/2 (Ni$^{2+}$) were observed. These peaks are similar to the observed in the pre-reaction samples. This indicates that CuO and NiO particles deposited over titanates do not undergo corrosion or reduction during the hydrogen evolution reactions. All of this information gives support about the stability of the samples and is similar with the previously reported in our group about composites prepared by solvocombustion and impregnated with CuO and NiO used for hydrogen evolution [40] where is shown the presence of nickel and copper oxidized species (as CuO and NiO) after the photocatalytic reaction.

b) X-ray diffraction

As it is shown in Fig. S5, XRD patterns of Ba$_3$Li$_2$Ti$_8$O$_{20}$ and Na$_2$Ti$_6$O$_{13}$ loaded with 2 w% of CuO exhibit similar reflections than the observed in the original samples; indicating no changes in the structure of the photocatalysts. Due to the low amount of CuO and NiO, no peaks attributed to these phases were identified in the diffractograms obtained of the samples before and after the reaction.

c) SEM

Fig. S6 shows the SEM images of the samples after the photocatalytic reaction. As can be observed in these images, the characteristic morphology of the materials was kept after the reaction, and the small particles of CuO and NiO remain coupled to the surface of titanates. A quantitative analysis through EDS was performed (Table S1), confirming that the load of co-catalyst was not affected during the reaction, and there were no losses of metal oxides into the solution.

Finally, it is important to remark that the materials prepared in this work only exhibited the evolution of hydrogen. Even when they have appropriate potential of the valence band to perform the oxidation of water, the experimental results did not show the evolution of oxygen. Theoretically, the
splitting of water should generate stoichiometric amounts of hydrogen and oxygen, however, the kinetics of the oxygen evolution is slower and more difficult compared to the hydrogen evolution, due to it needs the transference of 4 electrons, instead of 2, as it is in the case of hydrogen production. Additionally, due to its solubility, it is possible that a considerable amount of the evolved oxygen generated in the reaction remains dissolved in the water. Also, oxygen can be adsorbed in the surface of the photocatalyst. Due to the factors discussed, the detection of the photocatalytic oxygen evolved is particularly difficult.

Conclusions

Ba$_3$Li$_2$Ti$_8$O$_{20}$ and Na$_2$Ti$_6$O$_{13}$ isostructural phases were prepared by solid state and sol-gel methods. The photocatalysts showed stable activity under UV light for hydrogen evolution. Na$_2$Ti$_6$O$_{13}$ exhibited higher activity (120 $\mu$/mol/g) compared to Ba$_3$Li$_2$Ti$_8$O$_{20}$ (30 $\mu$/mol/g). The lower activity of Ba$_3$Li$_2$Ti$_8$O$_{20}$ was attributed to the distortion in the octahedrons due to the larger bond lengths in this phase, which increases the recombination rate in the material. Also, the characteristic 1D morphology obtained in the sodium hexatitanate phases played an important role in the photocatalytic activity, enhancing the charge separation of the charges through the 1D structure. Further, the activity of the tunnel structured titanates was improved 10 and 3.5 times in the case of Ba$_3$Li$_2$Ti$_8$O$_{20}$ and Na$_2$Ti$_6$O$_{13}$, respectively, with the incorporation of CuO nanoparticles as cocatalyst. The enhancement in the photocatalytic activity of the studied titanates was possible with the formation of an n-p heterostructure in the interface of n-type titanates and p-type CuO, promoting an improved separation, transference and utilization of the photogenerated charges in the photocatalytic reaction. In summary, the photocatalysts developed in this work exhibited competitive activities for hydrogen evolution compared to similar phases reported in literature.

Acknowledgments


Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2017.12.004

References

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